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Babcock & Wilcox

DISPERSED-PHASE ADDITIVE TESTS FOR SO_2 CONTROL,

LR:68:4078-01:9 (ES-9477)

PUBLIC HEALTH SERVICE

CONTRACT PH86-67-127

DECEMBER 10, 1968

RESEARCH AND DEVELOPMENT DIVISION

RESEARCH CENTER ALLIANCE, OHIO

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PROGRESS REPORT

JUNE 1, 1967 THROUGH JULY 31, 1968

PILOT PLANT INVESTIGATION OF THE POTENTIAL OF DIRECT LIMESTONE-DOLOMITE ADDITIVE INJECTION FOR CONTROL OF SULFUR DIOXIDE FROM COMBUSTION FLUE GASES

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By

R. C. ATTIG

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SUMMARY OF A

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Pilot plant tests have been made to evaluate the effectiveness of raw, hydrated and calcined limestones and dolomites injected into the flue gases to reduce sulfur dioxide concentration. The effects of additive fineness, temperature of injection and injection rate were also investigated for selected additives. The influence of limestone and dolomite on fly ash strength and on coal ash slag viscosity and fusion temperatures has been determined to evaluate the effect on ash deposition on furnace walls and in tube banks. The influence of additives on the ash collection properties as determined by bulk and in situ resistivity measurements has also been determined.

Raw additives were most effective at Port 1 (approximately 2300F), where the most effective (M-21831, a marl) removed 26% of the SO_2 when injected at stoichiometric rates [(Ca + Mg)/S]. A dolomite, M-21982 removed 47% of the SO_2 although injection rates were extremely high at more than 800% of the stoichiometric.

Hydrates were somewhat more effective than the raw stones at Port 1, and effectiveness did not decrease when they were injected into lower gas temperatures.

The hydrates as a class had greater specific surface areas than the raw limestone prepared in the normal manner. We believe this was one factor affecting their effectiveness, and tests with the raw additives indicated that increased fineness improved performance.

The additives will have varying effects on ash deposition depending on the amount used and on the properties of the additive and coal ash. For the materials tested thus far, we would expect that large quantities of additive would decrease the extent of wall slagging and produce soft deposits under normal operating conditions. However, the great dust loading may place a burden on ash-handling and soot blowing equipment.

Fly ash resistivity tests indicate that limestones and dolomites will make the fly ash more difficult to collect.

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PH-86-67-127

1.0 INTRODUCTION

An earlier summary progress report presented the results of 38 pilot plant tests made to investigate the effectiveness of limestone and dolomites in reducing the level of sulfur dioxide in flue gases. In that report, additive injection rates were computed on the basis of calcium only being reactive. This basis was used because information available at that time indicated that only calcium was effective in removing sulfur dioxide. With that assumption, the pilot plant tests indicated dolomites were more effective than limestones at the same injection conditions. The limited data available also showed that injection of limestones and dolomites at gas temperatures of about 2300F and slightly higher was more effective than injecting at temperatures below 2000F. In contrast, two dolomite hydrates were more effective at lower temperatures.

Since that time, more than 100 additional pilot-plant tests were made to evaluate the effectiveness of raw and calcined limestones and dolomites, as well as hydrated forms. The effects of additive fineness, temperature of injection, and injection rate were also investigated for a few selected additives. The influence of limestone and dolomite on fly ash strength, and on coal ash slag viscosity and fusion temperatures has been determined to evaluate the effect on ash deposition on furnace walls and in tube banks. The influence of additives on the ash collection properties as determined by bulk and in situ resistivity measurements has also been determined.

1.1 Ash Deposition-Background

One of the major objectives of this program is to evaluate the effect of selected additives on ash deposition on boiler surfaces. Ash deposition is a very complex phenomenon, and its occurrence and severity depend largely on the coal ash composition and the amount of coal ash. However, it can be strongly influenced by the method of firing, design of the boiler, soot blower equipment and the operating conditions.

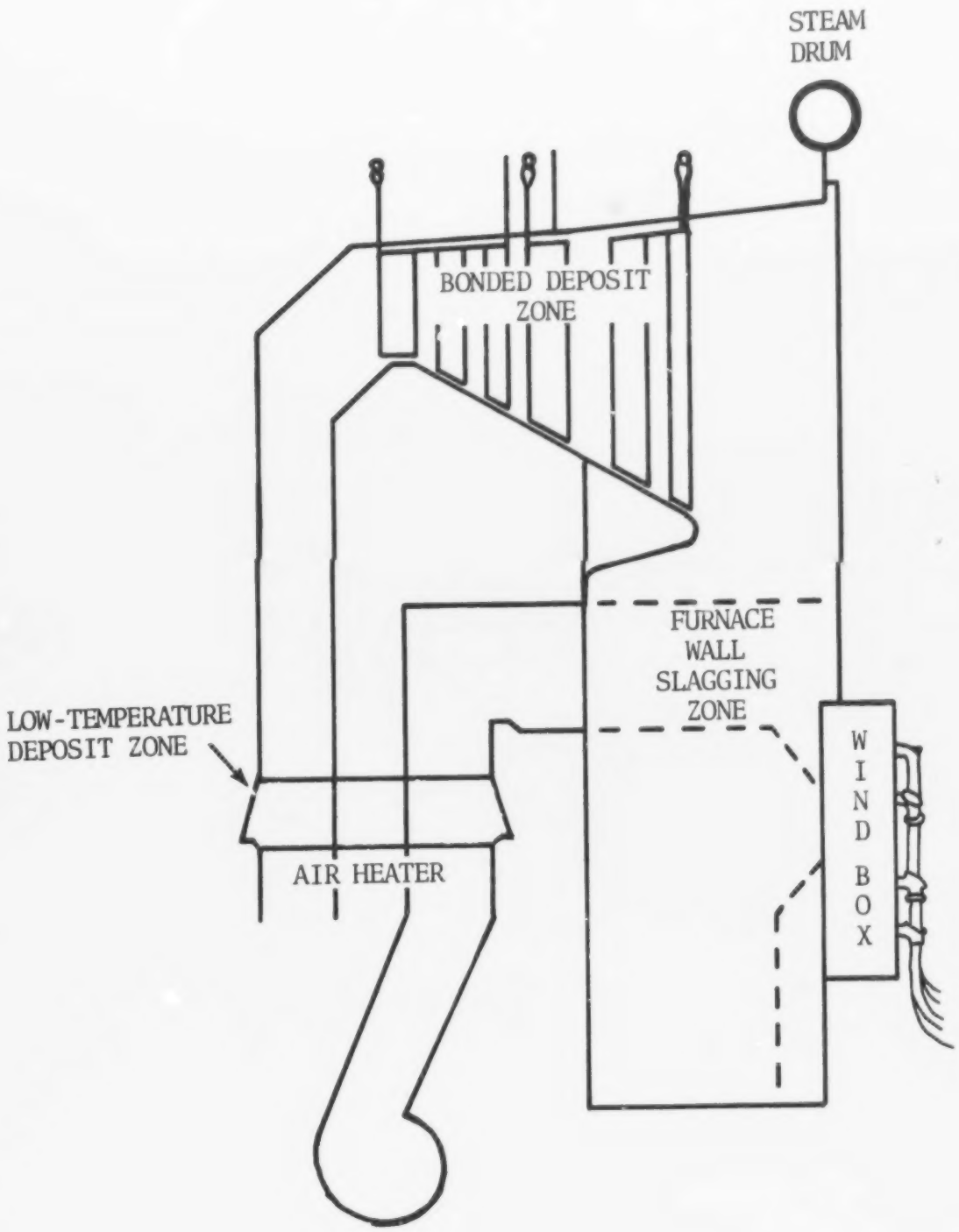
Ash deposits can be divided into three general types:

1. Fused-slag deposits which form on furnace walls and other surfaces exposed to predominately radiant heat transfer.
2. High-temperature bonded deposits which form on convection heating surfaces, especially the superheaters.
3. Low-temperature deposits which occur on low temperature surfaces such as the air heater and economizer.

The regions in which the deposits occur are shown on Figure 1.1.

Fused-slag deposits are usually associated with the physical transport of molten or sticky ash particles by the flue gases. Selective deposition of constituents can occur through condensation or deposition of species vaporized or decomposed by the flame can also occur. Condensation causes enrichment of certain elements, particularly in the cooler portions of the slag deposits, which is one factor making it difficult to predict the severity of slagging. In some cases, ash fusion temperatures provide an indication of the potential wall slagging problems that might be encountered with a particular coal. For example, coal ash with very high fusion temperatures will remain dry, and little or no deposit will form on furnace walls. However, for coals with lower ash fusion temperatures other factors

FIGURE 1.1. ASH DEPOSIT REGIONS IN A COAL-FIRED BOILER



are important. B&W has found that plastic slag is very difficult to remove from furnace walls. Thus, the temperature range over which the slag is plastic provides a guide to the extent of slagging that might be expected. Temperature differences between incipient melting (initial deformation temperature) and the fluid point are indicative of the plastic region, but the actual viscosity is the best measure.

The extent of high-temperature deposition varies greatly from coal to coal, with method of firing, with changes in operating conditions, and with the extent of furnace wall slagging. The ash concentration in the coal and the firing method (slag tap vs dry ash) will determine the dust burden being borne by the flue gases, and therefore strongly influence the rate of ash deposition. Of course, higher ash deposit rates will require greater cleaning capability for in service cleaning. Another important factor in deposition on tube banks is the hardness of the deposit, which is a function largely of the coal ash composition. The B&W Company has developed a test known as the sintering test which measures the strength of fly ash collected from an operating unit. Experience from a large number of utility boilers and from a variety of coals tested in the pilot plant described later show a definite relation between fly ash strength and fouling history.

The third type of deposit, which occurs on low-temperature surfaces, is usually associated with the condensation of sulfuric acid on surfaces at temperatures below the acid dewpoint. The deposits are normally mixtures of corrosion product and fly ash in varying proportions.

Moderate amounts of calcium and magnesium have been used successfully as boiler additives for low-temperature corrosion control. Limited success

s also been achieved in high-temperature deposition on oil and coal fired boilers. However, only a very limited amount of information is available on the effect of massive amounts of additive on furnace wall slagging and deposition, and much of this is conflicting.

2.0 EXPERIMENTAL

2.1 Pilot Plant Tests

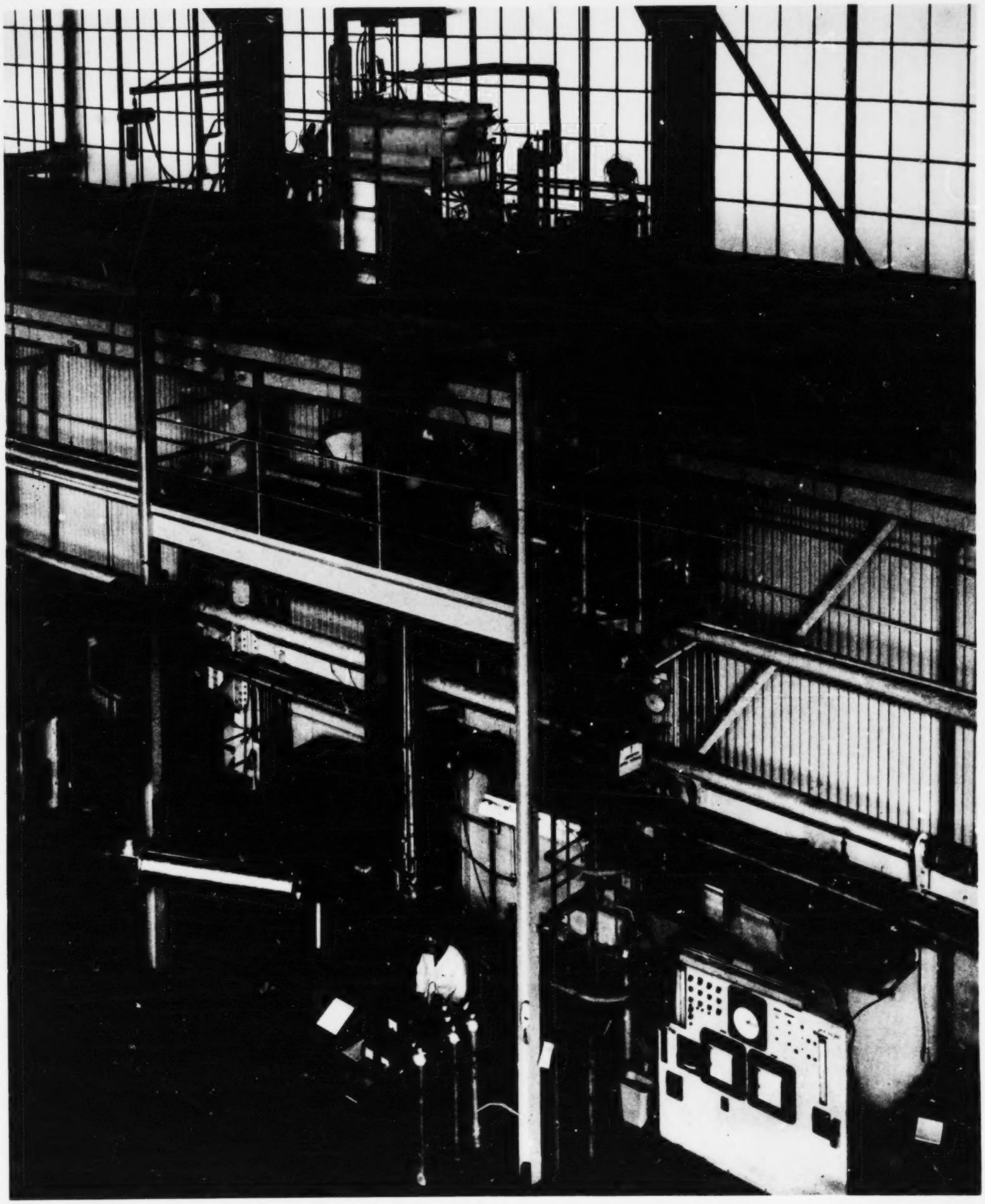
All tests have been conducted in a small pulverized-coal-fired pilot plant modified to permit the injection of an additive through any one of four ports located along the flue gas path. After the additive is mixed with the combustion gases and entrained particles of fly ash, the gas stream is cooled to about 500F in a boiler and then passes through a plenum housing a resistivity probe. A cyclone separator is used downstream of the plenum to clean up the gas stream prior to the SO_2 analyses, and to provide an ash sample for analysis. The SO_2 level is monitored by an infrared detector which is equipped with a recorder. A description of the pilot plant and auxiliary equipment is given below. The operation of this equipment is also described below and a more detailed description of the resistivity apparatus and SO_2 analytical equipment is given in the Analysis Section (6.0).

2.1.1 Coal Fired Pilot Plant

The pilot plant, shown on Figure 2.1, is designed to burn 3-20 lb of pulverized coal per hour under controlled conditions. These conditions include excess air, combustion temperature, residence time and simulate the conditions that exist in an actual boiler. The unit consists of the following major components: a coal feeding system, an externally heated combustion system, an additive feeding system, a water-cooled pressurized boiler, a gas clean-up and analytical system and fly ash resistivity measuring system.

A Vibra Screw Feeder delivers pulverized coal at a uniform rate to a stainless steel loop where it is mixed and circulated with primary air.

FIGURE 2.1. COAL FIRED PILOT PLANT

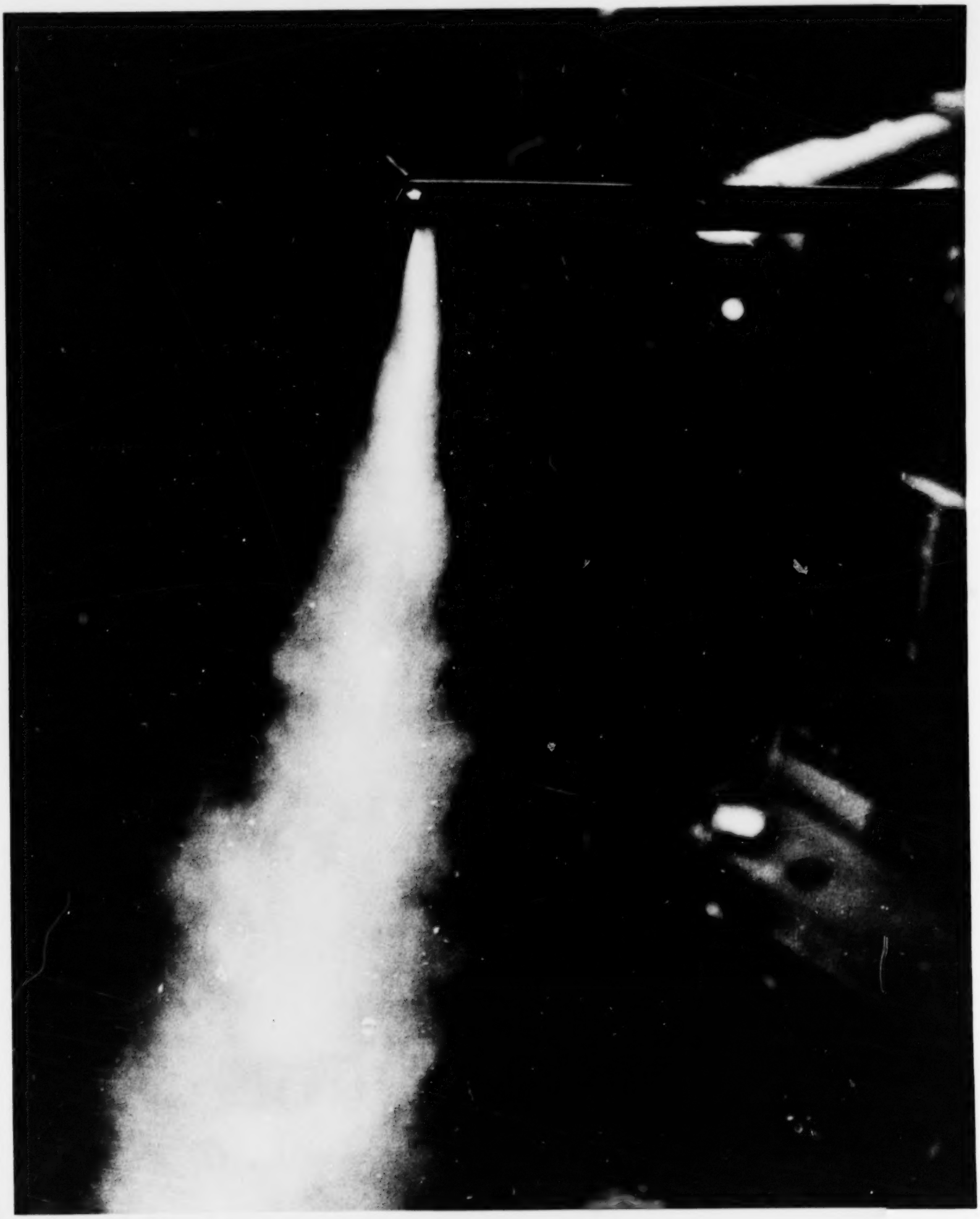


The coal is burned within a silicone carbide cylinder, which can be heated externally by an auxiliary natural gas furnace. The combustion gases and entrained fly ash pass into a vertical heat exchanger where they are cooled to approximately 500F. A water-cooled coil was also installed recently to drop flue gas temperature to 300F for resistivity measurements if desired. The resistivity of the fly ash is then measured in a plenum by means of a probe and control equipment supplied by Research-Cottrell. A cyclone ash collector is used to remove particles for analysis and to provide a clean gas sample for sulfur dioxide analysis.

The coal input can be controlled at any rate between 3 and 20 pounds per hour by varying the feeder screw speed. Primary and secondary air flows, indicated by pressure drops across orifices installed in the lines, make up approximately 15 percent and 85 percent of the combustion air, respectively. The oxygen concentration in the flue gases, as measured by a Bailey oxygen recorder, is held constant by manually adjusting air flows. Flue gas, water, and air temperatures are continuously recorded throughout the test period.

The additive is fed by another Vibra Screw Feeder into an air stream where it is aspirated into the flue gases through one of four ports. These ports, identified throughout this report as No. 1, No. 2, No. 3 and No. 4 correspond to the gas temperatures of about 2300F, 1900F, 1700F and 1500F respectively, depending on coal firing rate and other factors. The air used to convey the additive normally makes up 20-30% of the total combustion air and cools flue gases several hundred degrees. The additive feeder is equipped with two screw sizes. These, combined with a variable speed drive provide a range of additive feed rates of from less than 1 pound an hour to more than 10 pounds per hour. The additive is distributed in the flue gas stream by means of a nozzle designed to produce a conical pattern. Figure 2.2 shows the distribution of the additive as it leaves this nozzle.

FIGURE 2.2. DISTRIBUTION OF ADDITIVE LEAVING INJECTION NOZZLE



2.1.2 Test Procedure

The coal selected for our pilot plant tests was obtained from the normal fuel supply for Colbert Steam Plant of the Tennessee Valley Authority. This coal was randomly divided among a number of containers for handling and storage convenience, and a representative sample was obtained for analysis.

Additives used by the National Air Pollution Control Administration in their tests along with several other additives obtained by the B&W Company have been tested. They are prepared by pulverizing in a small impact mill to pass a pulverizer classifier screen.

To date, more than 100 pilot plant tests have been made to determine the reactivity of raw, calcined, and hydrated additives. Additives were injected into various regions of the pilot plant ranging from addition with the coal to as low as 1400F.

The procedure followed when operating the pilot plant is briefly outlined below:

1. The auxiliary furnace is preheated overnight by firing natural gas. Natural gas is then fired the following morning in the coal combustion chamber until the desired furnace operation temperatures are reached.
2. The natural gas line is then removed and coal is burned at a steady rate of 8 to 10 lb per hour with approximately 15% excess air.
3. Limestone or dolomite, in the desired quantities is injected into the flue gases through one of the four ports. A number of tests

were also made in which the additive was thoroughly mixed and fed with the coal and several using nitrogen instead of air for injection.

4. Following instrument calibration, the SO_2 level is monitored through the coal firing period. Continuous infrared analysis is the normal method of SO_2 analysis and a wet chemical technique (KIO_3) is used as a check.
5. Resistivity measurements (beginning in April when the equipment was installed) are made during injection of numerous additives as well as during coal firing only.
6. The fly ash and additive mixture are collected in a cyclone separator at the boiler outlet. A number of the mixtures have been analyzed for calcium, carbonate, and sulfur levels and by X-ray diffraction to identify crystalline constituents. Sintered strengths are also being measured for fly ash only and for selected mixtures.
7. Coal samples are collected for each test date to provide a measure of the sulfur input. Coal ash and selected additives are mixed for ash fusion temperature and viscosity measurements.

During the injection period, the excess air level increases to about 40% because of the air used to convey the additive.

Tests have been made to determine the sulfur dioxide concentration under a variety of conditions, including:

1. Base tests - no additive injected
2. Injection of various limestones and dolomites

3. Injection of other chemical forms (hydrated and calcined products of limestones or dolomites)
4. Effect of particle size (specific surface)
5. Effect of injection temperature
6. Effect of injection rate
7. Effect of excess combustion air.

Throughout this report stoichiometric calculations are based on the mole ratio:

$$\frac{\text{Calcium + Magnesium in Additive}}{\text{Sulfur in Coal}}$$

More detailed descriptions of several of the analytical techniques are given later in the Analysis Section.

3.0 RESULTS

3.1 Coal Analysis

The analysis of the coal selected for this study is shown on Table 3.1. It is a relatively high sulfur coal (4.3%) with an ash content of slightly over 15 percent. Fusion temperatures are relatively low.

3.2 Comparison of Carbonate

A summary of results for the raw additives is given on Tables 3.2 and 3.3. Maximum removal of SO_2 with stoichiometric injection of dolomites and limestones was only 26%. This was obtained with a marl M-21831 and represents the average of two tests. A dolomite, M-21982, removed 19% of the SO_2 when injected at nearly 200% of stoichiometric (Test 68-03-06). With injection rates of more than 800% of stoichiometric the dolomite removed 47 percent of the SO_2, the maximum removed thus far. The effect of stoichiometric ratio for three additives is shown on Table 3.4 and on Figure 3.1.

3.3 Effect of Specific Surface

Increasing the surface area/fineness of dolomite, BCR 1337, improved its effectiveness, as shown on Table 3.5 and on Figure 3.2. Furthermore, finer additives such as M-21831 and the hydrates reacted with more SO_2 than the coarser limestones and dolomites. Figure 3.3 shows the effect of introducing two size fractions of greater than and less than 325 mesh additive with the coal and through Port 1.

TABLE 3.1. COAL ANALYSIS

East Diamond Mine, West Kentucky

Sample No.	B-22791
Proximate Analysis - Dry - %	
Volatile Matter	37.4
Fixed Carbon	47.4
Ash	15.2
Btu/# - Dry	12,150
Chlorine - Dry - %	0.02
Sulfur Forms - Dry - % as S	
Pyritic	2.7
Sulfate	0.1
Organic (Diff.)	1.5
Total	4.3

Ash Fusion Temperature - F

	Red.	Oxid.
A (ID)	1940	2240
B (ST, Sp)	1990	2300
C (ST, Hsp)	2060	2340
D (FT, 1/16")	2340	2460
E (FT, Flat)	2370	2510

Ultimate Analysis - Dry - %	
Carbon	67.5
Hydrogen	4.6
Nitrogen (Calc.)	1.3
Sulfur	4.3
Ash	15.2
Oxygen (Diff.)	7.1
Ash Composition - %*	
SiO_2	39.
Al_2O_3	16.
Fe_2O_3	27.
TiO_2	0.5
CaO	9.
MgO	0.3
Na_2O**	0.6
K_2O**	2.2
SO_3 (Grav.)	3.4

*Analysis by emission spectrograph
**Analysis by flame photometer

TABLE 3.2. SUMMARY OF PILOT PLANT TEST RESULTS

LIMESTONES

RUN NO.	B&W SAMPLE NO.	EXCESS OXYGEN-%	INJECTION RATE % OF STOICH (Ca + Mg)/S	ADDITIVE SURFACE AREA CM^2/gm	SO_2 REMOVED-%
67-09-06	M-21571	6.1	113	1760	10
67-09-07	21602	5.6	114	5400	12
67-09-11	21593	6.0	115	6740	8
67-10-04	21591	6.0	91	3870	8
67-10-06	21588	5.9	73	4890	2
67-10-09	21597	5.6	84	4450	6
67-10-10	21598	6.0	101	2450	13
67-10-11	21600	6.4	96	4730	13
67-10-12	21599	6.5	96	3980	16
67-10-13	21601	6.6	97	2970	10
67-10-14	21831	6.4	80	11180	29
67-10-15	21606	6.9	79	2250	11
67-10-16	21607	6.9	78	2010	8
68-06-05	21831	7.0	137	11180	22
68-03-17	21993	6.4	130	2520	20
68-04-01	22006	5.5	103	2210	7
68-04-04	22008	7.3	113	2740	3
68-05-07	22005	5.5	100	2350	11
68-05-08	22053	5.8	110	4560	4
68-05-10	22046	7.2	106	1650	4
68-06-01	22046	5.9	89	1650	7
68-06-03	22081	5.2	105	4360	11
68-06-05	22081	5.7	101	4360	4
68-06-18	22055	5.7	108	3720	9
68-06-19	22052	5.0	112	4510	10
68-07-01	22058	5.8	97	3510	12
68-07-02	22059	5.5	113	4250	10
68-07-06	22060	5.8	96	2368	7
68-07-11	22061	5.5	112	1480	7
68-07-12	22060	5.7	102	2360	8
68-07-13	22063	5.5	124	4220	11
68-07-14	22062	5.7	119	3800	7
68-07-15	22066	5.9	116	2430	9
68-07-16	22067	5.8	112	3700	10
68-07-20	22069	5.5	119	2410	6
68-07-24	22065	6.0	122	2350	12
68-07-25	22073	5.5	108	--	9

TABLE 3.3. SUMMARY OF PILOT PLANT TEST RESULTS

DOLOMITES

RUN NO.	B&W SAMPLE NO.	EXCESS OXYGEN-%	INJECTION RA. % OF STOICH (Ca + Mg)/S	ADDITIVE SURFACE AREA CM^2/gm	SO_2 REMOVED-%
67-10-07	M-21595	4.5	111	2110	6
68-04-05	22004	5.9	119	2050	10
68-04-06	22002	6.2	106	3130	12
68-04-08	22003	6.4	128	2200	10
68-04-09	22002	6.7	107	3130	13
68-05-05	22000	6.0	132	2100	11
68-05-09	22054	5.3	104	3470	10
68-05-11	22047	6.2	124	2040	6
68-06-14	22048	5.5	118	3330	8
68-06-15	22049	5.6	118	2630	13
68-06-17	22050	5.2	117	3140	17
68-07-19	22068	5.5	114	2790	9
68-07-21	22070	5.7	117	3000	6
68-07-22	22071	5.7	124	2170	6
68-07-23	22064	5.9	124	1960	14
68-07-26	22074	5.6	113	--	13

TABLE 3.4. EFFECT OF STOICHIOMETRIC RATIO

SAMPLE	TEST NO.	SPECIFIC SURFACE CM^2/g	STOICHIOMETRIC RATIO	SO_2 REMOVED -%
DOLOMITE M-21911 (BCR-1337)	67-10-02	2340	1.6	26
	67-10-03	2340	1.8	26
	68-02-06	1630	1.7	22
	68-03-15	2040	2.1	20
	68-02-14	1630	3.9	36
	68-02-15	1630	6.0	41
DOLOMITE M-21982 (BCR-1353)	68-10-08	2340	1.5	25
	68-03-06	1560	2.0	19
	68-02-11	1560	2.1	16
	68-03-04	1560	5.4	40
	68-03-05	1560	8.3	47
M-21993 LONGVIEW LIMESTONE	68-06-13	2520	1.1	11
	68-03-10	2520	1.3	15
	68-03-17	2520	1.3	20
	68-07-10	2520	2.6	22

FIGURE 3.1 SO_2 REMOVAL AT VARIOUS INJECTION RATES

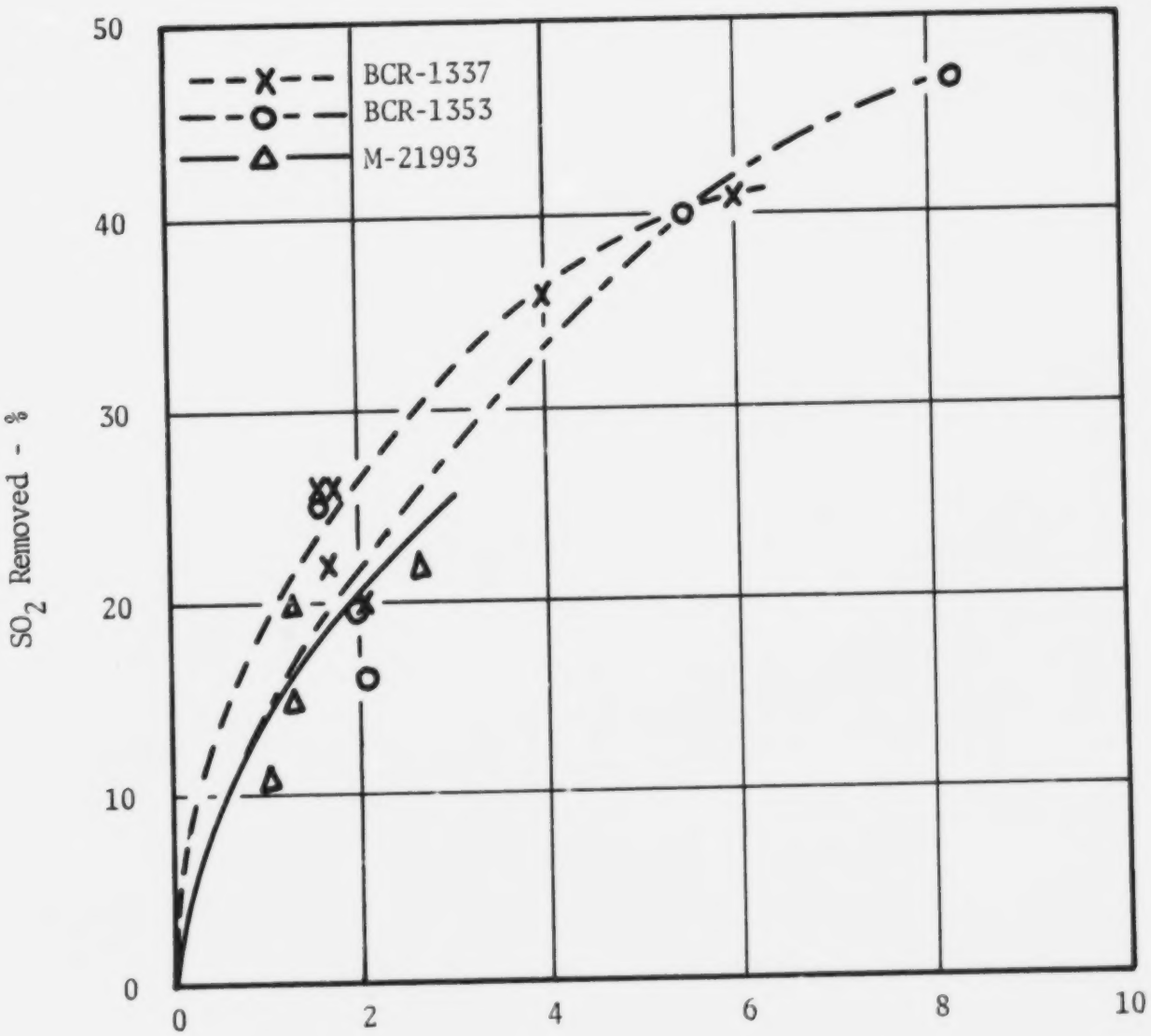


TABLE 3.5. EFFECT OF SPECIFIC SURFACE

(BCR 1337, Approx. 2x Stoich.)

Test No.	B&W Additive No.	Specific Surface cm^2/gm	SO_2 Removed %
68-03-13	M-21911-A	290	12
68-03-14	M-21911-B	610	15
68-02-06	M-21911	1630	22
68-03-15	M-21911-C	2040	20
67-10-02	M-21594	2340	26
67-10-03	M-21594	2340	26
68-03-01	M-21912	2360	21
68-03-02	M-21913	3330	21

TABLE 3.6. EFFECT OF EXCESS AIR

Oxygen at Furnace Outlet - %	Oxygen at Boiler Outlet - %	Injection Medium	SO_2 Removed %
3.0	6.0	Air	15 (average)
1.0	4.0	Air	10
0.2	3.0	Air	2
3.1	3.1	Nitrogen	13
1.1	1.5	Nitrogen	4

FIGURE 3.2. EFFECT OF ADDITIVE FINENESS ON SO_2 REMOVAL

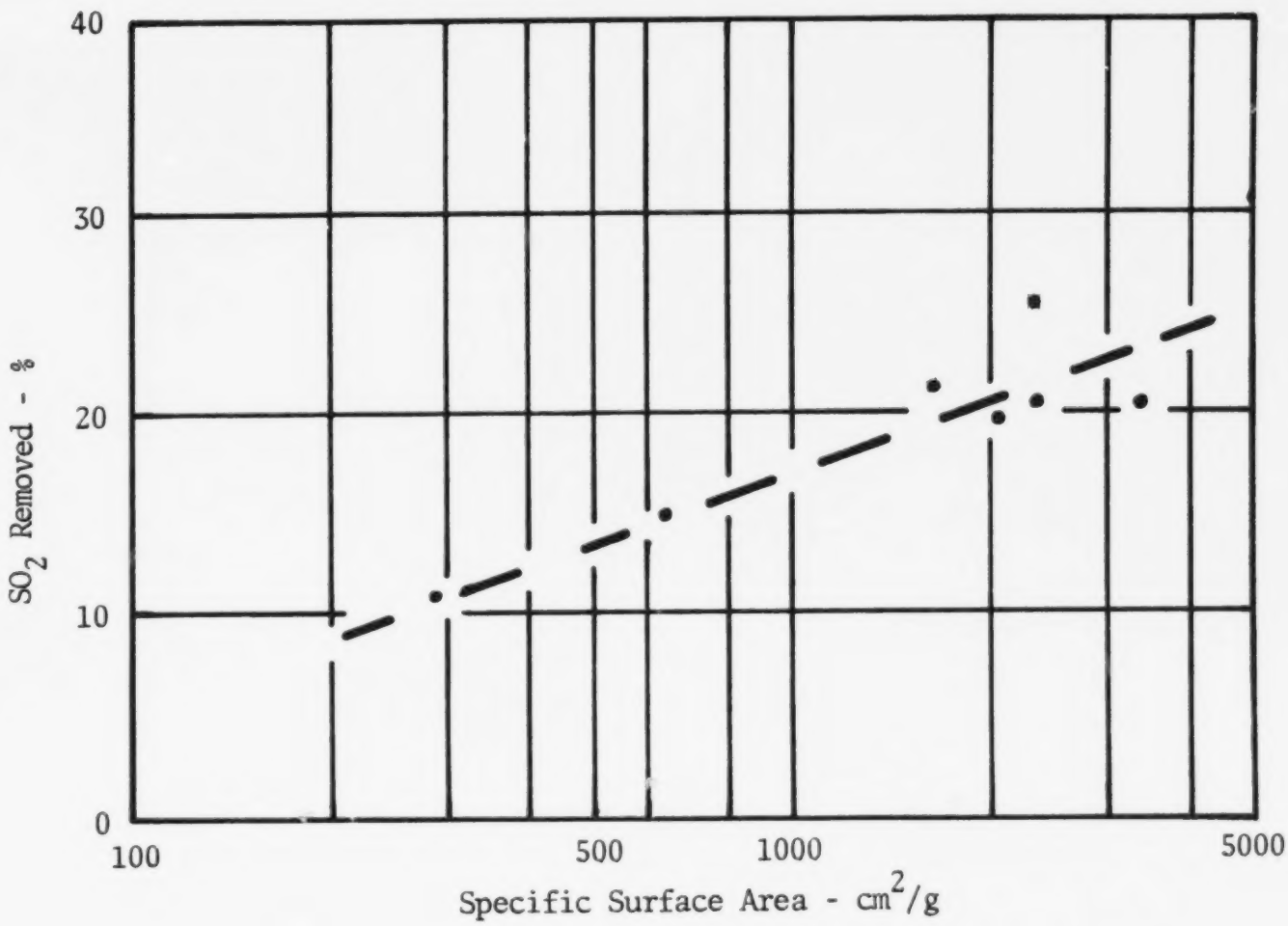
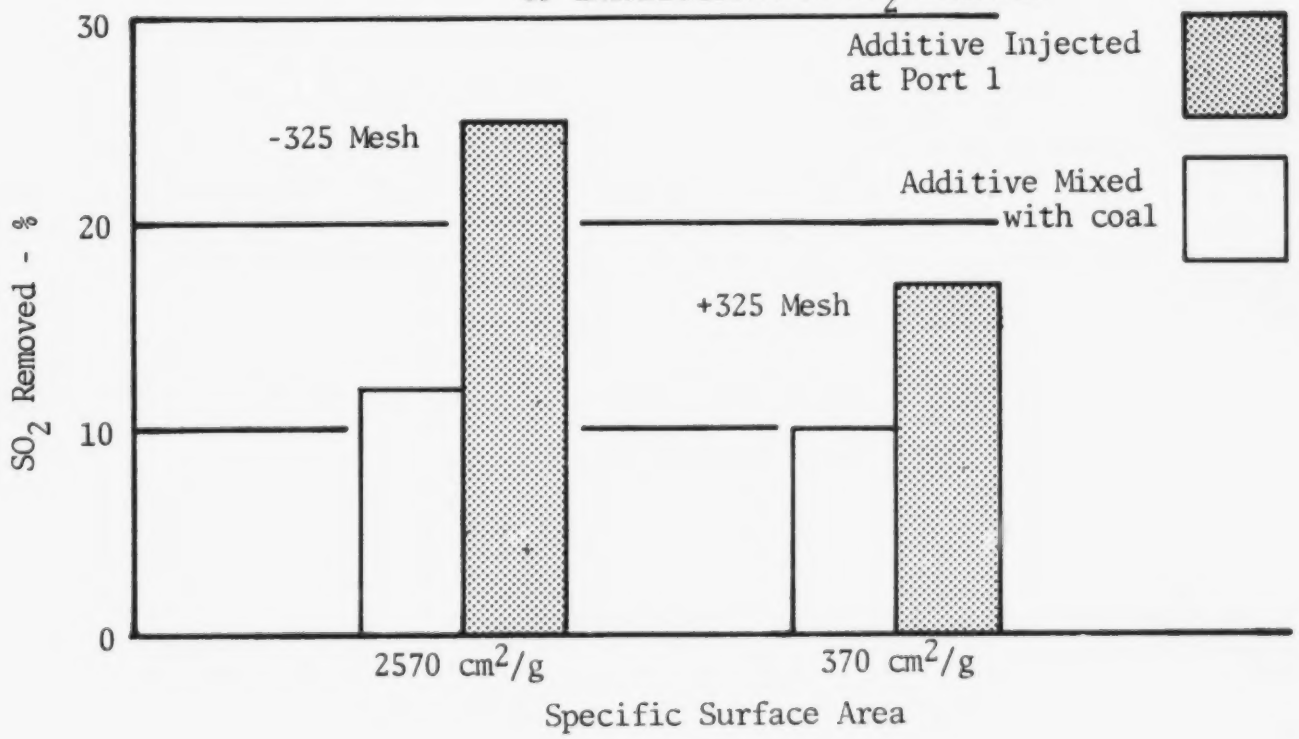


FIGURE 3.3. EFFECT OF ADDITIVE FINENESS AND POINT OF INTRODUCTION ON SO_2 REMOVAL



3.4 Effect of Gas Temperature at Injection Point

Figure 3.4 gives a summary of the average effect of injection temperature for a number of limestones and for dolomite BCR 1353 and a specific limestone M-21993. SO_2 removal is maximum when raw additives are injected through Port 1.

3.5 Effect of Excess Combustion Air

The effect of varying the combustion air/coal ratio, and injecting the additive with nitrogen instead of air is shown on Figure 3.5 and on Table 3.6.

3.6 Effect of Additive on Fusion Temperature

Ash fusion temperatures for mixtures of M-21831 and coal ash are shown on Figure 3.6. A mixture of 25% additive and 75% coal ash had a fluid temperature lower than that of the coal ash alone. Increasing the amount of this limestone raised the fusion temperatures. Figure 3.7 shows the effect of a limestone (M-21831) and a dolomite (BCR-1337) on the viscosity of the coal ash.

3.7 Effect of Additive on Sintering Characteristics

The sintered strength of the fly ash was reduced from 4600 psi to 36 psi at 1700F when M-21993 was injected at stoichiometric rates (See Figure 3.8).

3.8 Effect of Additives on Fly Ash Resistivity

In general, additives increase the resistivity of the fly ash, as shown on Figure 3.9, reproduced from a Research-Cottrell report.

FIGURE 3.4. EFFECT OF GAS TEMPERATURE AT INJECTION POINT

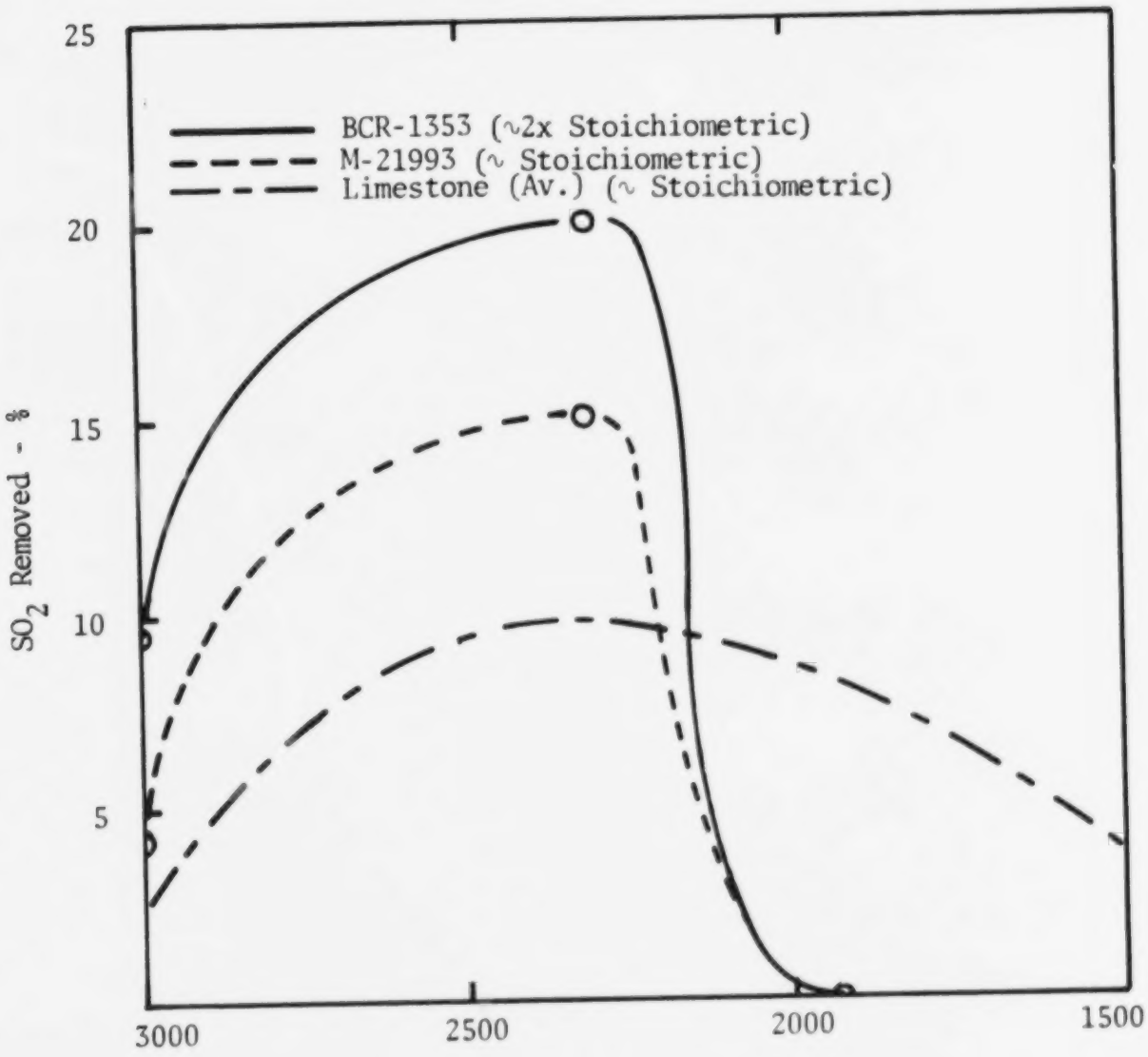


FIGURE 3.5 EFFECT OF COMBUSTION AIR-FUEL RATIO ON SO_2 REMOVAL

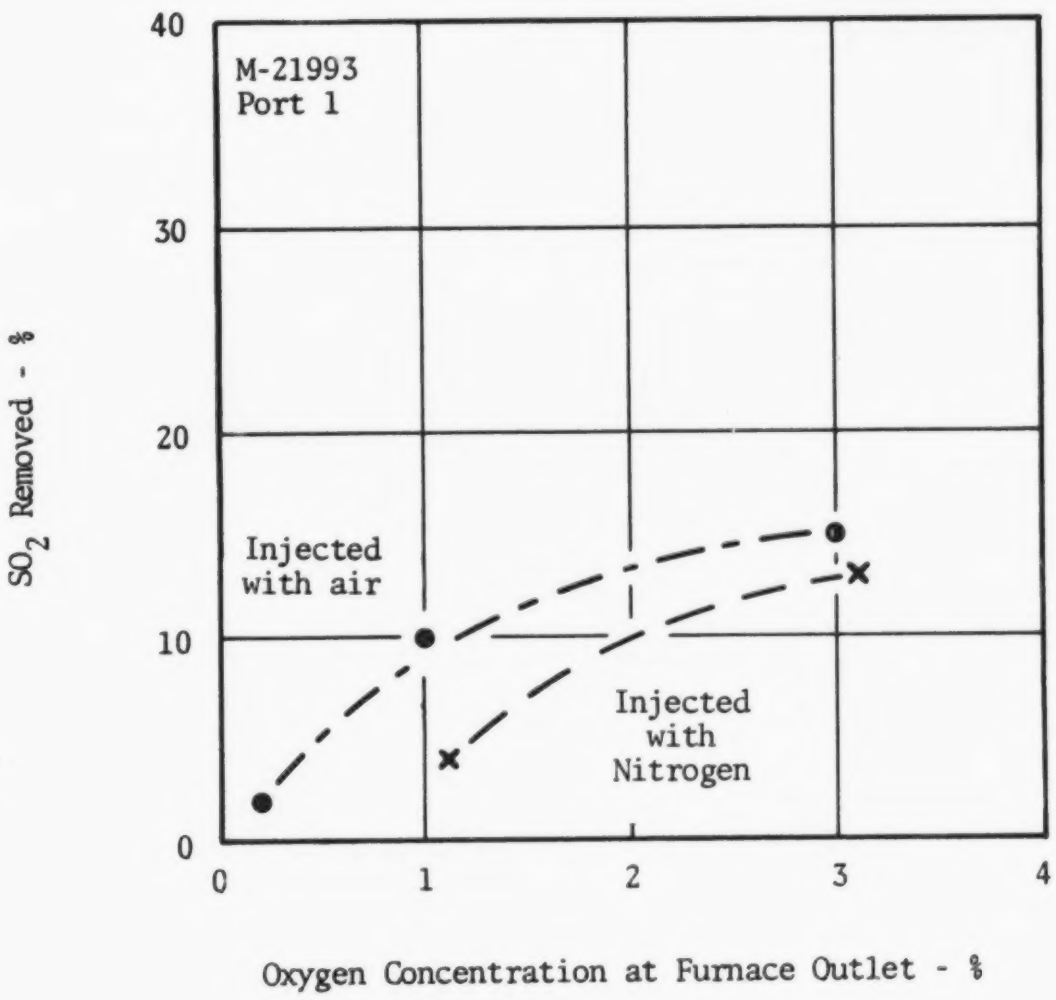


FIGURE 3.6. ASH FUSION CHARACTERISTICS OF
A MIXTURE OF COAL ASH AND M-21831

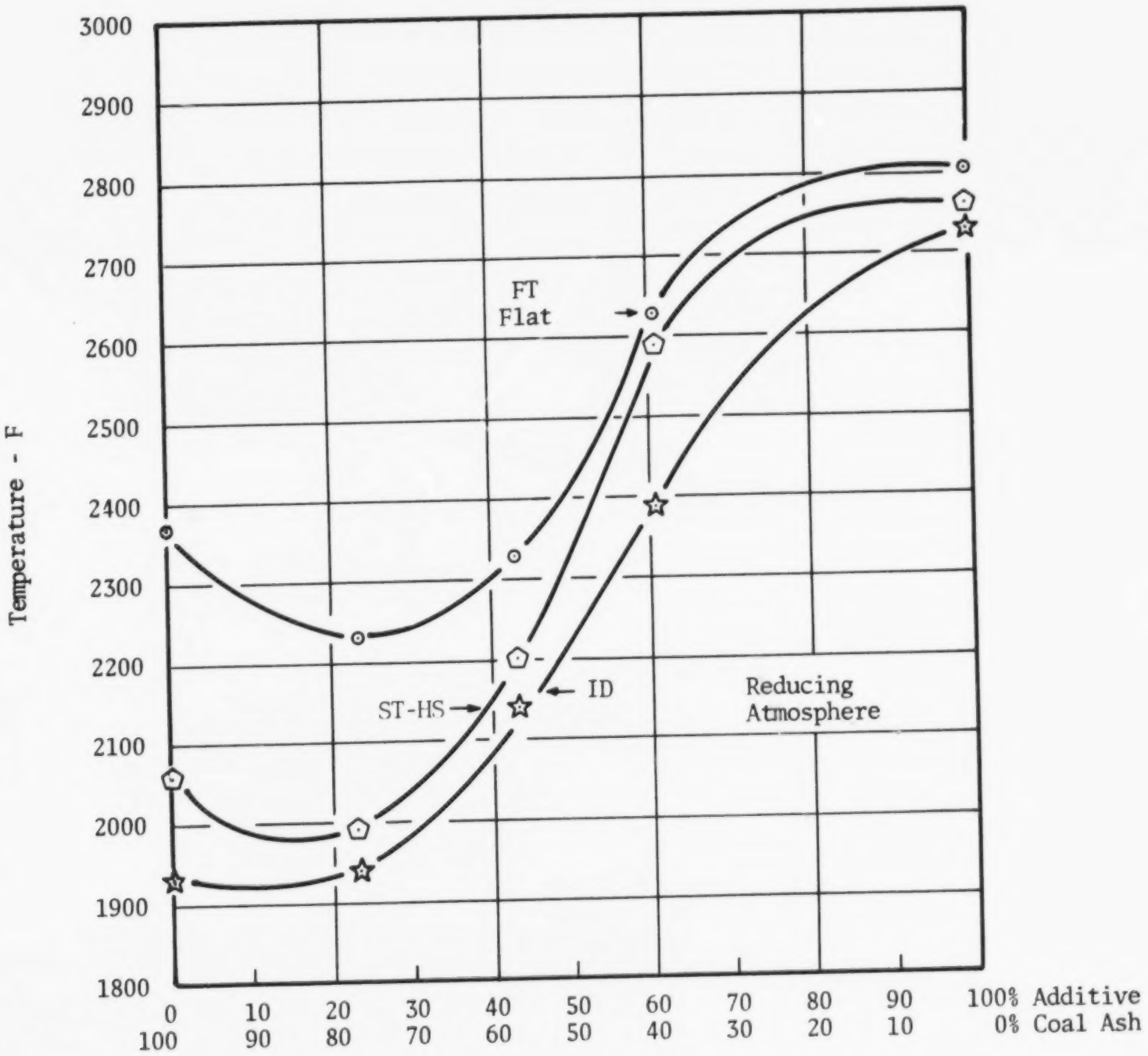


FIGURE 3.7. VISCOSITY - TEMPERATURE RELATIONSHIP

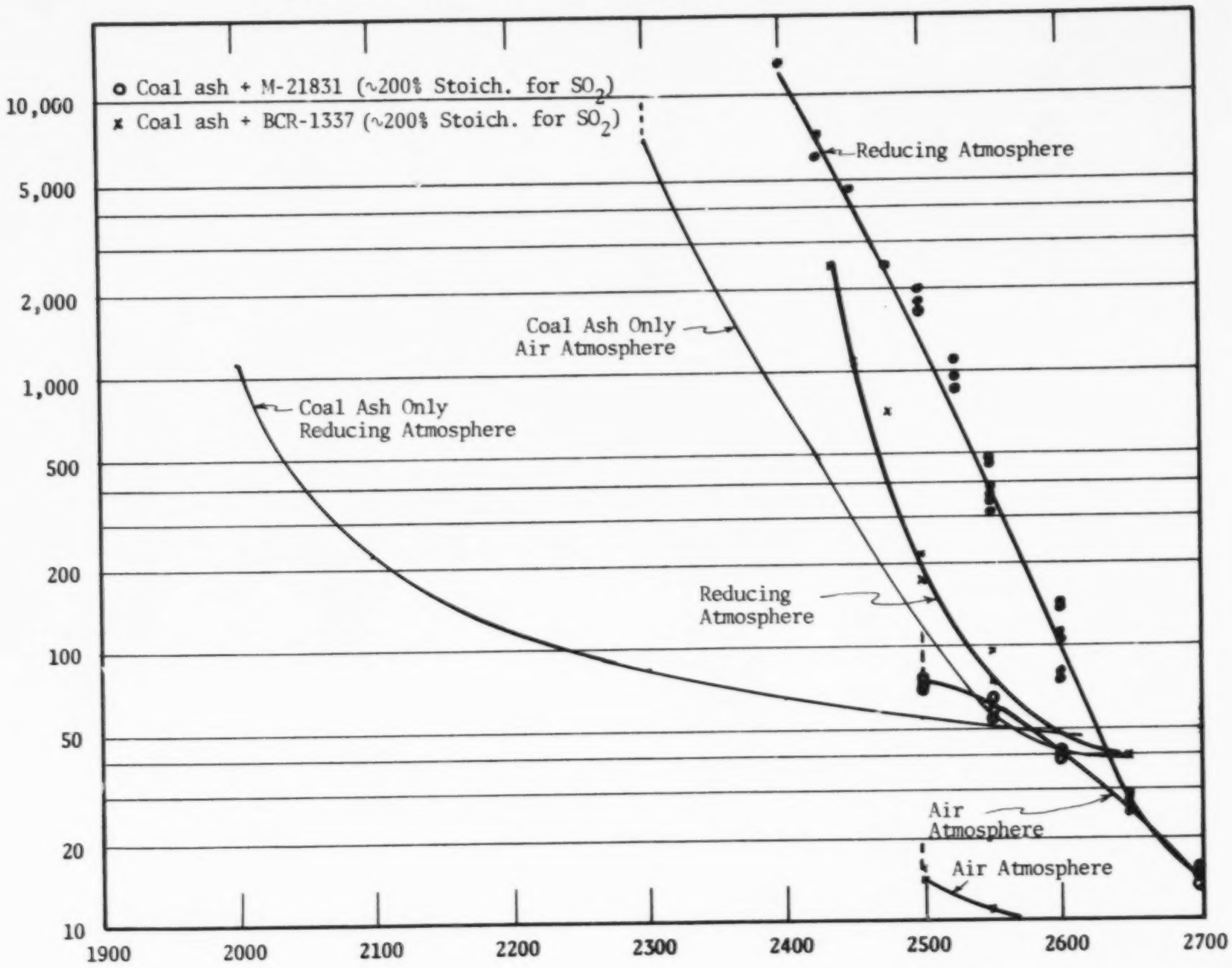


FIGURE 3.8. SINTERING CHARACTERISTICS OF FLY ASH FROM VARIOUS COALS

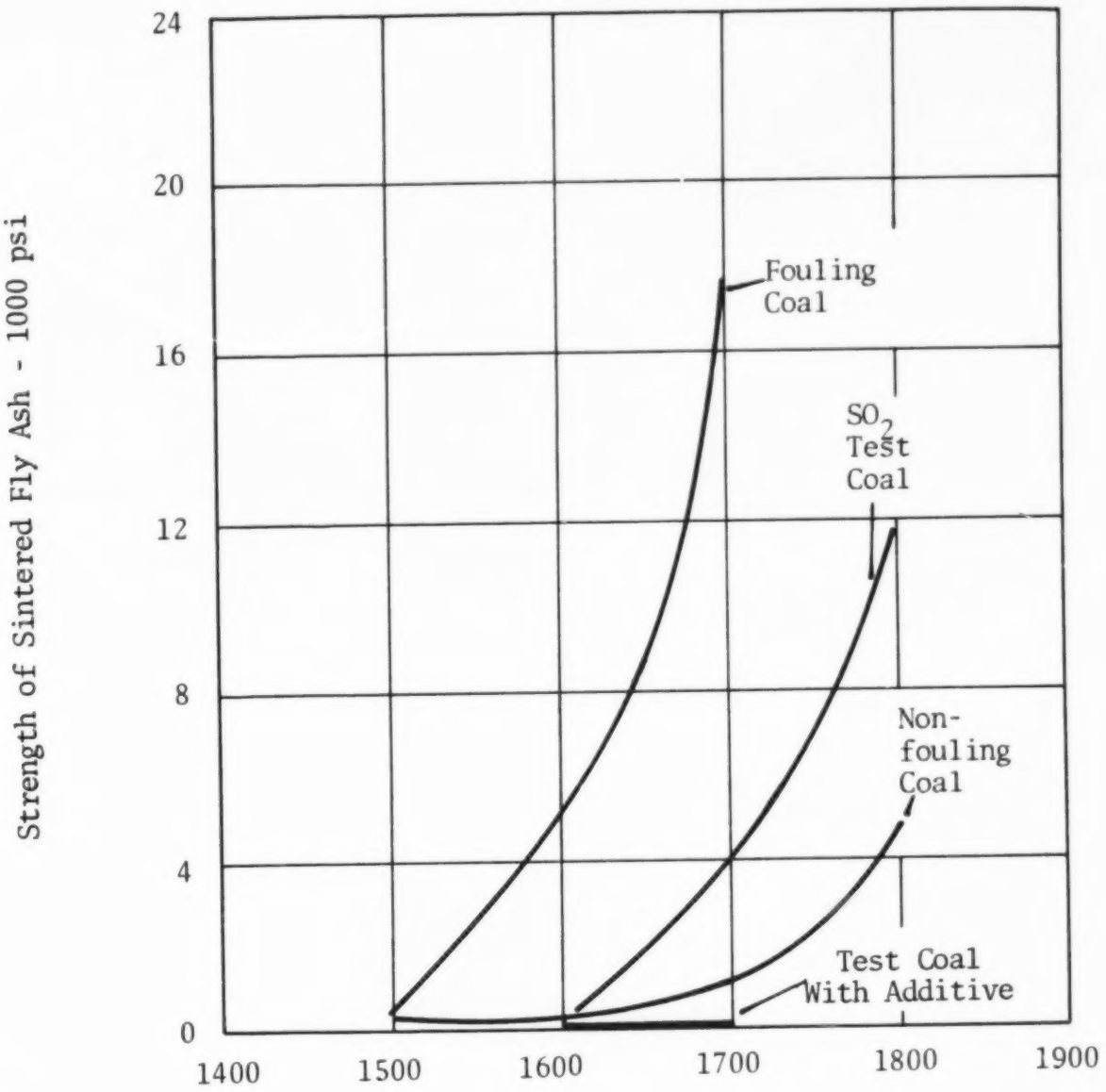
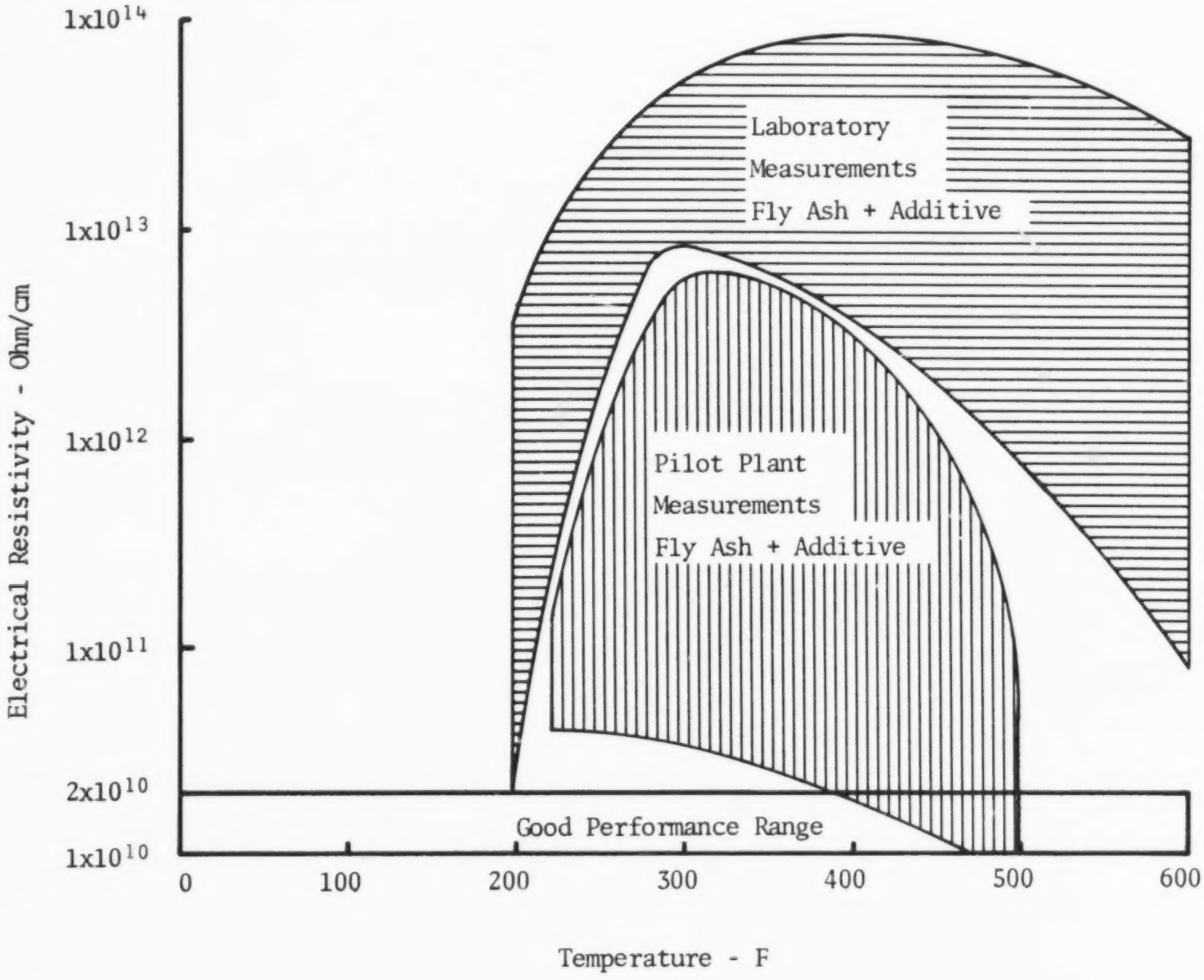


FIGURE 3.9. ELECTRICAL RESISTIVITY CHARACTERISTICS OF ADDITIVE-FLY ASH MIXTURES



4.0 DISCUSSION

4.1 Additive Reactivity

As noted earlier, the reactivity of raw limestones and dolomites injected at a stoichiometric ratio of 1 [(mole% Ca+Mg)/mole% S] is relatively low. By comparison, this is not greatly different from a number of full scale tests reported by other investigators. We have found that the performance can be improved by using finer additives, which will be discussed in detail later. Other investigations have attempted to relate additive reactivity to composition, but have not found a satisfactory correlation. A linear regression analysis was performed on the results earlier in our program, and only silica in the additive showed any relation to additive performance. Even here the correlation was very poor. We anticipate doing another analysis of this type after more samples are tested. Another factor affecting additive performance is the design of equipment. A comparison of factors that might affect performance in the pilot plant and extrapolation of these data to full scale equipment is given below.

The pilot plant was designed and modified as necessary to produce a fly ash with sintering characteristics similar to those of fly ash from a utility boiler. The total residence time, at approximately normal operating conditions, is within the range of utility boilers. Combustion temperatures, and excess air levels are among other parameters also similar to commercial practice. In some respects, differences do exist that may affect the total amount of SO_2 removed. These include additive distribution, gas recirculation, reaction with deposited additive, and residence time in the temperature zone for reaction with SO_2.

Overall, assuming the additive is well dispersed in the boiler flue gases, performance in the boiler should be somewhat higher than in the pilot plant. However, we would not expect a very large increase in most cases.

4.1.1 Distribution of Additive

Since the pilot plant is small, designing a distribution system for the additive was relatively simple. Conversely, a utility boiler furnace may have a cross section of several thousand square feet, making distribution more difficult. Thus, from the standpoint of additive distribution, performance in the pilot plant should be somewhat better than in the full scale boiler.

4.1.2 Recirculation of Additive Within Flue Gas Eddy Currents

The geometry of many B&W boilers has been model tested and the actual unit was subsequently designed to minimize eddy currents. The pilot plant is designed for unobstructed flow with essentially no areas for recirculation to take place. The net effect of this would be difficult to assess with the information now available.

4.1.3 Reaction with Deposited Additive

The pilot plant was designed to minimize deposition on internal surfaces to provide for maximum recovery of fly ash. In contrast, extensive heat transfer surface is provided in boilers in the form of tube banks, providing a large amount of surface for reaction between additive and SO_2. Much of this deposit would be at temperatures which numerous investigators have found to be optimum for removal of SO_2. Therefore, a utility boiler would provide for greater reaction between deposited additives and sulfur dioxide than does the pilot plant.

4.1.4 Residence Time

The total residence time in the pilot plant with an input of 100,000 Btu/hr at 115% total air is approximately 2.5 seconds. Gas temperature at the pilot plant outlet (before clean up) is normally about 550F without additive injection. Residence time between ports 1 and 4, corresponding to gas temperature of 2300F and 1500F respectively, is approximately half a second under the same conditions. By contrast, residence time between 2400F and 1400F in the boiler at Shawnee, where full-scale tests are planned, is about 1.5 seconds. Research by others has shown that in most instances, the greater residence time in this temperature range will result in higher levels of SO_2 removal. However, other factors such as the sensitivity of the stone to dead burning, additive distribution and fly ash properties may be important as well.

4.2 Additive Fineness

The use of finer additives appears to be one technique to improve the performance of an additive. The performance could probably be improved further with the finer additives if the problem of distributing the additives uniformly in the flue gases can be overcome. Very fine additives tend to form agglomerates consisting of numerous particles. Thus far, the so-called dispersants tested have given no significant improvement in handling. The surface areas of several normal size fractions used in the fineness tests are given below.

Mesh Size	Specific surface cm^2/gm
+ 200 (174μ)	290
- 200 + 325 (74 x 44μ)	610
- 325 (-44μ)	2,040

Another important factor is the energy requirement and, therefore, the cost, of preparing additives with surface areas as large as 10,000 to 15,000 cm^2/gm.

4.3 Effect of Gas Temperature at Injection Point

We mentioned earlier that additives can be injected into the pilot plant through one of four ports, or they can be mixed and fed with the coal. Mixing with the coal permits the additive to pass through the flame allowing for maximum exposure to flue gases at high temperatures. This high temperature exposure apparently reduces the reactivity of the additives in the flue gases. However, tests that have been reported in monthly reports indicated that reacted additive-fly ash mixtures retain high levels of reactivity in a SO_2 water slurry, even under these conditions.

The flue gas temperature at Port 1 is approximately 2300°, the highest temperature available for injection of limestones. Reactivity of raw dolomites and limestones has been higher at this port than at the others or when the additives were mixed with the coal. It is quite possible that injection into a temperature higher than 2300F will increase the additive effectiveness. This will be difficult to check with the present furnace configuration, although it may be possible to inject the additive through a port at the top of the furnace, using a water cooled injection nozzle.

4.4 Effect of Catalysts

The overall reaction occurring when a raw additive is introduced includes several steps.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + 1/2\ O_2 + SO_2 \rightarrow CaSO_4$$

The kinetics of these reaction steps are difficult to predict in a system where distribution is unknown, where competing reactions can occur and where temperatures and, thus, equilibrium concentrations are changing rapidly. There is some thought that the oxidation of SO_2 to SO_3 may be rate controlling and therefore some emphasis has been placed on catalysts to promote this step. Any catalyst that would increase the speed of the rate controlling chemical reaction would improve the additive effectiveness. Therefore some effort has been expended to evaluate the effectiveness of catalysts.

One material that has been used as a catalyst for this reaction is iron oxide, which is readily available and relatively inexpensive. The Longview additive supplied by TVA was used by TVA in preparing mixtures with three levels of iron oxide. As we understand it, the mixtures were prepared by milling the limestone and rouge together to provide adequate mixing. The mixtures removed more SO_2 than the limestone itself. Unfortunately the milling also produced very high surface areas, which tended to cloud the results. Future tests of this type are planned, using mixtures with surface areas similar to that of the base additive.

4.5 Role of Magnesium

There is considerable evidence that magnesium is active in removing SO_2, contrary to some other researchers' findings. This is supported by three important factors. First, low calcium magnesites removed 10% of the SO_2 in the flue gases. Second, dolomites are about as effective as limestones at equivalent injection rates assuming both calcium and magnesium are reactive. Finally, magnesium sulfate has been tentatively identified in the reacted additive-fly ash mixture by differential thermal analysis. The identification

technique now consists of holding the reacted additive-fly ash over a water bath in a high humidity atmosphere for 16 hours, then running a differential thermal analysis of the product. High magnesium additives produce a mixture that exhibits an endothermic peak at approximately 150C in the same region as both $CaSO_4 \cdot 2H_2O$ and $MgSO_4 \cdot 7H_2O$. Fly ash mixtures collected when low calcium additives were injected do not exhibit this peak. Calcium sulfate hydrates to the $CaSO_4 \cdot 2H_2O$ form slowly and after 24 hours the $CaSO_4$ has absorbed only enough water to form the hemihydrate whereas $MgSO_4$ hydrates rapidly. The calcium sulfate hemihydrate does not have an endothermic peak at 150C.

4.6 Additive Form

The hydrates appear to be more effective than the raw additives, although only limited results are available thus far. A summary is given in Table 4.1. The optimum injection temperature range for the hydrates appears to be 1900F-1500F, whereas the raw stones are almost completely ineffective at these temperatures. This is probably due in part to the lower temperatures required for decomposing the hydrates compared to carbonates. However, this does not explain their reactivity below 1400F, where equilibrium favors formation of carbonate rather than sulfate. Adsorption has been suggested as a possible mechanism.

Precalcined additives have been ineffective in reducing SO_2 concentration, as shown for the Longview limestone in Table 4.1 below. The calcination procedure is very important in establishing the reactivity of limestones and dolomites. It has been suggested that flash calcination may produce a more reactive material than slower calcination at low temperatures.

TABLE 4.1. SULFUR DIOXIDE REMOVED - %

Chemical Form	Injection Port No. 1	No. 2	No. 3	No. 4
Longview Limestone Base				
Carbonate (M-21993)	15	0	0	0
Hydrate (M-21992)	13	-	22	22
Calcined (M-21981)	4	4	-	-
Dolomite Base				
Hydrate (M-21848	23	-	-	22
Dihydrate (M-21849)	18	-	27	27

We mentioned earlier that results with the very fine additives such as the hydrates have been inconsistent. It may be possible to achieve higher SO_2 removal and more consistent results with better distribution of additives. Dispersants are being sought and added to the materials to overcome this problem, but with little apparent success.

4.7 Ash Deposition

We pointed out in the Introduction that the disposition of ash on furnace walls and tube banks is a complex phenomenon, dependent on many factors including fuel properties and boiler operating variables. Empirical tests such as sintering, fusion and viscosity characteristics do provide guidelines that are valuable in establishing boiler and cleaning equipment design parameters. However, coal for a power plant is frequently obtained from numerous mines and coal properties can vary from hour to hour, and from one burner to another. It is also difficult and sometimes impractical to monitor and control operating conditions at each burner to assure uniform

operation. Therefore, findings of this investigation should be combined with continuous measurements and observations of furnace operating conditions, coal ash composition and ash deposition during the full scale tests.

Based on our laboratory observations for the West Kentucky coal tested additives would have varying effects on the fusion characteristics. Figure 3.6 showed that addition of enough M-21831 to react stoichiometrically with SO_2 would reduce the temperatures indicative of various stages of melting measured by the ash fusion temperature determination. Greater quantities would increase the fusion temperatures as would additions of BCR-1337, a dolomite. The temperature range of plastic slag ($\sim$500 poise to solid slag) would be smaller with additions of both M-21831 and BCR-1337, as shown on Figure 3.7. This would indicate a smaller zone at potentially severe slagging. Changes of fuel/air ratio, which would affect the gas composition over the melt, would also have less effect on the mixtures than on the coal ash slag alone.

The question of how much additive will codeposit with the coal ash is difficult to answer, but would depend on where the additive is injected. The potential effect on furnace wall slagging would obviously depend on this factor as well as the composition of the additive and coal ash. Specific conditions will need to be identified and several assumptions made to evaluate the overall effect of the additives on wall slagging.

Deposits on superheater and reheater tubes would be softer (see Figure 3.8) and therefore easier to remove with the use of additives while firing the East Diamond coal. However, the amount of solid material will increase compared to that normally handled. The actual increase, as a percentage of the fly ash normally being borne by the flue gases, will depend on the type of firing (stoker, slag tap or dry ash) as well as the additive injection rate. The load on ash removal and handling equipment will be greater and this should be taken into consideration.

5.0 CONCLUSIONS

5.1 Additive Reactivity

The reactivity of raw dolomites and limestone was generally low. Increasing the fineness improves the additives' performance but for raw limestones and dolomites as well as hydrates the very fine product required for maximum performance is difficult to feed at a uniform rate and disperse into the flue gases because of the tendency to agglomerate.

Optimum injection temperature determined thus far for raw additives corresponds to Port 1 which is approximately 2300F. Temperatures somewhat higher than this may improve performance although mixing with the coal gave poor results.

Hydrates appear to be more reactive than the raw additives and at present a lack of uniformity of performance appears to be due to the difficulty in feeding and dispersing the additive. The hydrates are also more effective when injected into lower gas temperatures, perhaps because of the lower temperature required for decomposing compared to the carbonates.

We have tentatively identified magnesium sulfate (as $MgSO_4 \cdot xH_2O$) in the reaction product by differential thermal analysis. Therefore, it appears that the reaction $MgO+SO_2+1/2\ O_2 \rightarrow MgSO_4$ occurs as does the reaction of calcium with sulfur dioxide.

5.2 Ash Deposition

Based on the tests to date, we would expect additives to have differing effects on ash deposition depending on the nature and amount of additive injected. Viscosity and ash fusion studies indicate that additions of limestone and dolomite tend to reduce the plastic region of the slag, thus restricting the severe slagging zone. However, the molten zone does occur

at lower temperatures when small quantities of additive are combined with the ash. With larger amounts of additive the slag is molten over a very narrow temperature range and at higher temperatures than the original coal ash, thus, slagging would be less severe.

Ash deposits in convection banks would tend to be softer with additives than without, in the amounts examined thus far. Calcium sulfate, particularly if it is allowed to get wet during outages or similar periods, can produce very hard deposits, however. Therefore, it will be imperative to quickly remove any deposit formations with frequent, regular sootblower operation. The massive dust burden may prove difficult to handle by ash handling equipment and in areas where the ash accumulates.

Regardless of the method, the laboratory approach provides only empirical guidelines and the boiler should be carefully observed during full scale trials to confirm these observations. Because selective deposition does occur in deposits, it also would be advisable to obtain and analyze deposits from various gas temperature regions of the boiler to determine the amount of additive appearing in deposits.

5.3 Electrostatic Precipitation

Both in situ and bulk resistivity tests indicate that the fly ash mixture will be more difficult to collect at normal temperatures (~300F) when additive is injected.

6.0 ANALYSES

6.1 Chemical and Physical Analyses

The coal is analyzed by standard ASTM methods including proximate, ash fusion temperatures, and ultimate. In addition, the ash composition is determined by emission spectrograph and flame photometer and the chloride level was measured. A sample of coal is taken daily for sulfur analyses.

The composition of the additives is determined by wet chemical and emission spectrographic techniques. Specific surface measurements are made using the Lea-Nurse method.

Samples of fly ash, reacted additive mixtures are collected, and the sulfur, carbonate, calcium levels are determined. The crystalline constituents are determined by X-ray diffraction analyses. Differential thermal analyses have also been made on a number of mixtures, chiefly to determine if this technique was capable of detecting magnesium sulfate.

Other methods of analyses are utilized as required to provide specific information.

6.1.1 Fly Ash Resistivity Apparatus

The Research-Cottrell portable resistivity apparatus is designed to measure the resistivity of dust suspended in flue gases under actual temperature and gas conditions. The control unit and the resistivity probe are shown on Figures 6.1 and 6.2. The probe consists of a small electrostatic point-plane cell at the end of a probe, with adapters to attach to various sample fittings. A small plenum was fabricated and installed at the outlet of the pilot plant to accommodate the probe. The control unit is provided to supply the necessary voltage and the metering equipment.

FIGURE 6.1. POWER SUPPLY AND CONTROL EQUIPMENT FOR RESISTIVITY PROBE

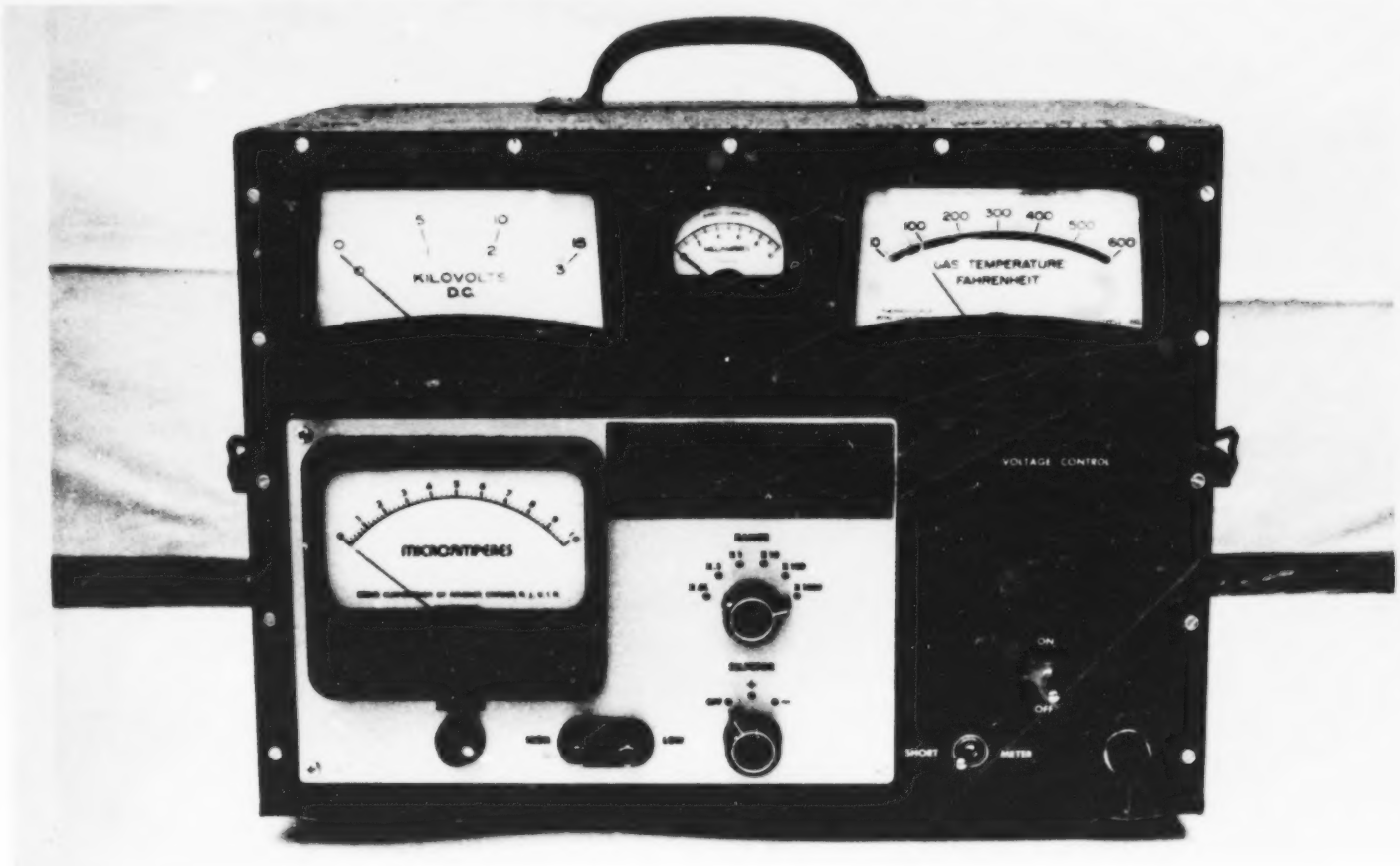
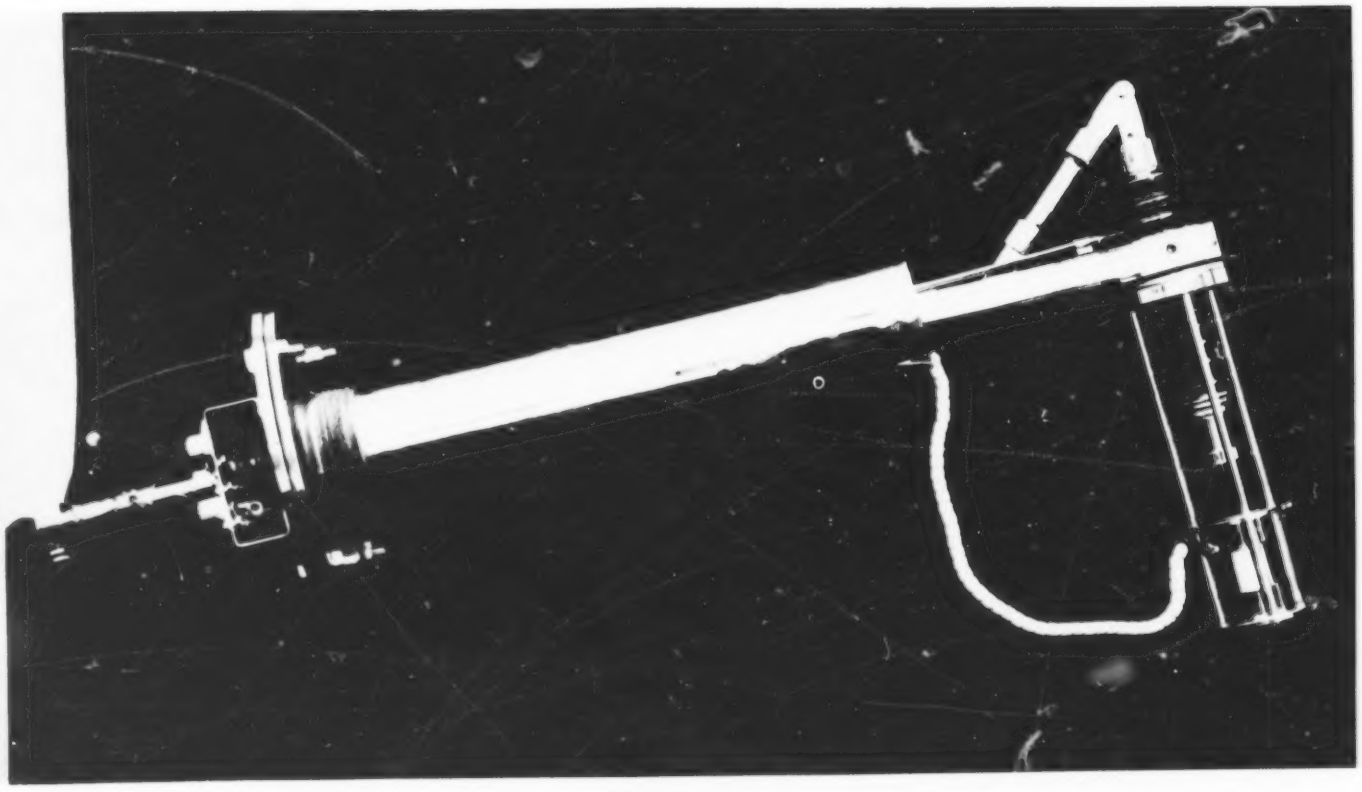


FIGURE 6.2. FLY ASH RESISTIVITY PROBE

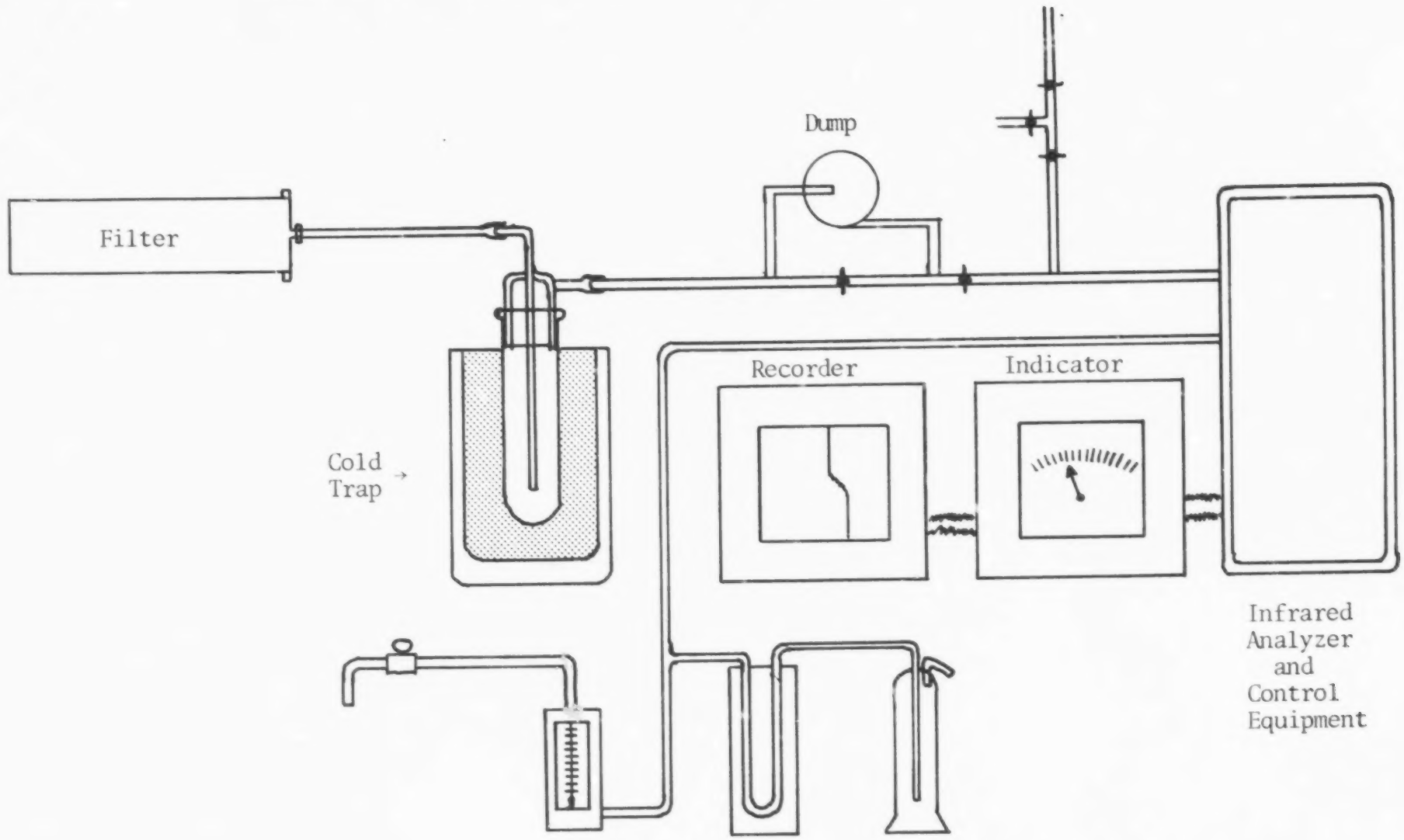


The resistivity of the fly ash or fly ash-reacted additive mixture is measured by placing the probe in the flue gas stream and applying a potential of approximately 7000 volts for 30 minutes to allow a layer of dust to precipitate on the bottom plate. A disc is then lowered gently into the deposit and the current flow is measured at several voltages. After the dust layer thickness is determined, the resistivity of the deposit layer can be calculated.

6.1.2 Sulfur Dioxide Analytical System

A Beckman Model 315 infrared analyzer is used to continuously monitor the SO_2 level in the combustion flue gases. This unit is equipped with a Bristol strip chart recorder to provide a permanent record of the SO_2 level. The gas cleanup system and the present arrangement is shown on Figure 6.3. The system now consists of a filter downstream of the cyclone separator, a cold trap to dry the flue gases followed by a plug of Kaolin wool. The gases are then moved through an IR detection cell, after which they pass through a flow meter to a spring-loaded relief valve which maintains a constant, low, positive pressure on the system. The gas is then vented to the atmosphere. A manometer is installed at the SO_2 analyzer to measure pressure at the analyzer. The infrared instrument can be bypassed and SO_2 concentration determined by absorption in a potassium iodate solution as a check on the IR instrument. The IR instrument was supplied with factory calibration curves over the range of SO_2 levels between 0 and 6000 ppm and it is calibrated with standard gases on days when pilot plant tests are made.

FIGURE 6.3. SULFUR DIOXIDE ANALYTICAL SYSTEM



6.2 Coal Ash Slagging and Fouling Evaluation

As mentioned briefly before, several techniques are used to estimate the slagging and fouling that might be encountered while injecting large quantities of additives. These methods are outlined briefly below.

6.2.1 Ash Fusion Temperatures

The terms used to identify ash fusion temperatures are described below. They refer to the melting characteristics of coal ash as determined in a gas fired furnace and include the four points determined in the standard ASTM designation: D1857-66 T. In addition to the ASTM temperatures, the Babcock and Wilcox Company determines the point identified as FT (Flat).

Symbol	Definition	ASTM Symbol
IT	Initial Deformation Temperature	IT
ST	Softening Temperature - (Spherical)	ST
HT	Softening Temperature (Hemispherical)	HT
FT (1/16")	Fluid Temperature-fused mass ~1/16" on plaque	FT
FT (Flat)	Fluid Temperature-fused mass, flat on plaque	--

A more complete description is given in the ASTM methods for Gaseous Fuels, Oil and Coal, Part 10, March 1968, p. 345. The ASTM method is tentative and was accepted in its present form in 1966.

6.2.2 Sintering Test

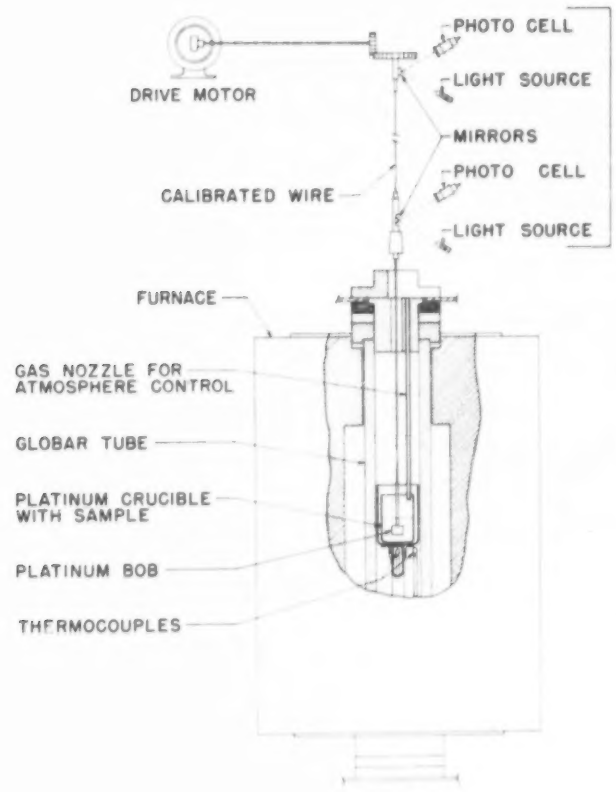
The fly-ash samples or mixtures of fly ash and reacted additive collected from the ashing furnace are passed through a 60-mesh U. S. Standard screen to remove essentially all particles of slag, and then ignited at 900F to remove any carbon that might be present. The ignited material is then reduced to a 100-mesh size and cylindrical specimens (0.6 in. diameter by 0.75 in. long) are formed in a hand press at a pressure of 150 lb. per sq. in. Six specimens are heated at each of several temperature levels for 15 hours. Thus, if the sintered strength is desired for three temperatures, a total of 18 specimens is required.

After the specimens have cooled slowly in the furnace, they are removed, measured, then crushed in a standard metallurgical testing machine. The sintered or compression strength is then computed from the applied force and cross-sectional area of the sintered specimen. The average strength of at least six specimens is used as the strength of the sintered fly ash at a particular sintering temperature.

6.2.3 Slag Viscometer

A diagram of the slag viscometer is shown on Figure 6.4. The method used by the Research Center to measure viscosity in the high-temperature range consists of measuring the forces that oppose the rotation of a bob submerged in a molten mass. The bob is suspended in the material by a calibrated wire which is rotated by a motor drive. When the bob is rotated at a constant speed, the wire twists by an amount proportional to the force opposing its rotation. The amount of twist is measured and recorded as the time interval between impulses from light beams reflected from two mirrors attached to the top and bottom of the wire.

FIGURE 6.4. HIGH TEMPERATURE SLAG VISCOMETER



The viscosity determination for wall slagging investigations is normally conducted in an air atmosphere. Since the oxidation level of the iron has a pronounced effect on the viscosity, it is sometimes desirable to make a viscometer run in a reducing atmosphere. For this purpose, a small gas nozzle is provided to introduce a mixture of hydrogen and nitrogen in place of air over the melt. The procedure for determining the viscosity is the same. In preparation for a viscosity measurement, the coal ash is heated to a fluid point. The slag is then cooled at selected temperature increments and viscosity measurements are made after the slag has been held at temperature for 30 minutes. Additional points are measured at specific temperatures to determine if the slag has reached equilibrium.

In order to determine the oxidation level of the iron, samples of the melt are obtained by inserting a small platinum probe, and breaking off the slag which freezes on it.

7.0 FUTURE WORK

The emphasis for this project will be on developing information for limestones being considered by TVA for their full scale injection tests. The optimum conditions will be determined for the more effective of these limestones. Additional work is planned for other additives as well, particularly on finer grinding and injection temperatures above 2300F. The effect of recycling reacted additive and the reacted additive after hydration as well as the effectiveness of catalysts will be investigated. Several coals of varying sulfur contents and ash composition will also be fired while additives are injected. The analyses of additives and reacted mixtures will be continued, and we will investigate the possible formation of calcium silicates. Reactivity of several of the reacted mixtures in a water slurry will be investigated.